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(A) Base oil for lubricating oil and lubricating oil composition containing said baid oil.

© A base oil for lubricating oil, a lubricating oil composition containing the base oil and a phenol-based antioxidant and/or an organomolybdenum compound, and also an additive for a base oil for lubricating oil, consisting of a phenol-based antioxidant and an organomolybdenum compound are disclosed. The base oil and the lubricating oil composition containing the base oil are stable against NO_xgas and are useful for use in internal combustion engines. The additive, when added to a base oil, provides a lubricating oil which is stable against NO_x gas and can be used effectively in a NO_x gas atmosphere.

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BASE OIL FOR LUBRICATING OIL AND LUBRICATING OIL COMPOSITION CONTAINING SAID BASE OIL บบ พ.ศ. การสา เก็บ**าร์** บบ กรรมกำหลัก ฮาก การ การสา การ

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1. Field of the Invention

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77 4 76 2 15 The present invention relates to a base oil for lubricating oil, a lubricating oil composition containing the base oil, and an additive for lubricating oil. More particularly, it is concerned with a base oil which is used as a lubricating oil stable in a nitrogen oxide (NO_x) gas atmosphere by itself; or is used to prepare such a 😘 💢 😘 stable flubricating oil in combination with suitable additives, a lubricating oil composition containing the 1 in the sabove base oil, and further with an additive for the general base oil for lubricating oil.

The term "lubricating oil" as used herein means a lubricating oil for use in internal combustion engines.

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In general, part of a combustion gas in internal combustion engines passes through between a piston and a cylinder, and leaks out into a crank case as a blow-by gas. Since this combustion gas contains a high concentration of NO_x gas, it deteriorates a crank case oil (internal combustion engine oil).

In recent years, cars equipped with a reduction catalyst such as a three-way conversion catalyst as a 20 countermeasure of exhausted gas regulations have been increasingly produced, and thus internal combustion engines are now operated under more severe conditions of high speed and high power. As a result, the concentration of NO_x gas in combustion gas leaking out into the crank case tends to increase.

Moreover, from a viewpoint of energy saving, it is promoted to make the car body lighter, and thus the and crank case is miniaturized. With this miniaturization, the amount of the crank case oil is decreased.

For the aforementioned reasons; "the concentration" of NOx gas in the crank case foil is markedly increased, and thus the crank case oil is greatly influenced by NO_x gas. With the conventional internal combustion engine oils containing zine dithiophosphate (Zn-DTP) and a detergent dispersant, abnormal degradation such as the formation of black sludge will occur in a short time.

Thus it has been desired to overcome the above problems and to provide a base oil or lubricating oil 30 which is stable in a NO_x gas atmosphere. On the other persons and the property of the stable in a NO_x gas atmosphere.

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CONSUMMARY OF THE INVENTIONS OF THE INVENTIONS OF THE PROPERTY OF THE PROPERTY

An object of the present invention is to provide a base oil which is stable in a NOx gas atmosphere and can be used as a stable lubricating oil for a long time.

Another object of the present invention is to provide a lubricating oil composition which is stable in a NO_x gas atmosphere and can be used without degradation for a long time.

Still another object of the present invention is to provide an additive for the general base oil, which produces a lubricating oil stable in a NO_x gas atmosphere.

Other objects and advantages of the present invention will become apparent from the following explanation. 3 30 30

The present invention relates to a base oil for lubricating oil, characterized by having a kinematic viscosity as determined at 100°C of 2 to 50 centistokes (cSt), an aromatic content (% CA) as determined by ring analysis of not more than 2% and a viscosity index of at least 75. For convenience of explanation, this Is hereinafter referred to as the "first invention".

The present invention further relates to a lubricating oil composition containing the base oil of the first invention and a phenol-based antioxidant and/or an organomolybdenum compound. This is hereinafter referred to as the "second invention".

The present invention further relates to an additive for the general base oil for lubricating oil, consisting of a phenol-based antioxidant and an organomolybdenum compound. This is hereinafter referred to as the la a Marcillon "third invention". . See 19 8 1

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DESCRIPTION OF PREFERRED EMBODIMENTS

The viscosity at 100°C of the base oil of the first invention is in the range of 2 to 50 cSt, preferably 3 to 20 cSt. If the viscosity is less than 2 cSt, the evaporation loss is undesirably large. On the other hand, if it is in excess of 50 cSt, the power loss due to viscosity resistance is too large.

The aromatic content of the base oil of the first invention is not more than 2% and preferably not more than 1%. If the aromatic content is in excess of 2%, degradation in a NO_x gas atmosphere is undesirably marked.

It is preferred for the base oil to have such characteristics as required for the usual lubricating oil to be used in internal combustion engines, for example (1) proper visesity characteristics. (2) good stability against oxidation. (3) good detergency and dispersancy. (4) good rust resistance and corrosion resistance. (5) good low temperature fluidity, and so forth. Specifically, it is more preferred for the base oil to have a viscosity index of at least 75, particularly at least 80, a suffir content of not more than 100 ppm, particularly not more, than 50 ppm, a total acid value of 0, 5 mg KOH/g, and a pour point of not more than -10°C, particularly not more than -20°C, most preferably not more than -30°G.

As the base oil of the first invention, various mineral oils and synthetic oils can be used as long as they have the above specified properties.

Representative examples of the mineral oil which can be used as the base oil of the first invention include a purified oil which is obtained by purifying a distillate oil by the usual method, said distillate oil 20 having been obtained by atmospheric distillation of a paraffin base crude oil or an intermediate bas crude oil, or by vacuum distillation of a residual oil resulting from the atmospheric distillation, and a deep dewaxing oil which is obtained by subjecting the above purified oil to deep dewaxing treatment. In this case, the process for purification of the distillate oil is not critical, and various methods can be employed. Usually, the distillate oil is purified by applying such treatments as (a) hydrogenation; (b) dewaxing (solvent 25 dewaxing or hydrogenation dewaxing), (c) splvent extraction, (d) alkali-distillation or sulfuric acid treatment, and (e) clay filtration, alone or in combination with one another, it is also effective to apply the same treatment repeatedly at multi-stages. For example, (1) a method in, which the distillate oil is hydrogenated, or after hydrogenation, it is further subjected to alkali distillation or sulfuric acid treatment. (2) a method in which the distillate oil-is hydrogenated and then is subjected to dewaxing treatment, (3) a method in which the distillate oil is subjected to solvent extraction treatment, and then to hydrogenation treatment. (4) a method in which the distillate oil is subjected to two-or three-stage hydrogenation treatment, or after the two or three-stage hydrogenation treatment, it is further subjected to alkali distillation or sulfuric acid rinsing treatment, (5) a method in which after the treatment of the distillate oil by the methods (1) to (4) as described above, it is again subjected to dewaxing treatment to obtain a deep dewaxed oil, and so forth can be employed.

In the practice of the above methods, it suffices that processing conditions be controlled so that the resulting oil has a kinematic viscosity at 100°C and an aromatic content both falling within the above-specified ranges.

A mineral oil obtained by deep dewaxing i.e., deep dewaxed oil is particularly preferred as the base oil of the present invention. This deep dewaxing is carried out by solvent dewaxing under severe conditions, catalytic hydrogenation dewaxing using a Zeolite catalyst, and so forth, and the severe conditions.

As well as the aforementioned mineral oil, synthetic-oils such as alkylbenzene, polybutene and poly(α-olefin), or mixtures thereof can be used as the base oil of the first invention.

The base oil of the first invention can be used as a lubricating oil for internal combustion engines by itself, because it exhibits sufficiently high stability against NO $_{x}$ gas. The stability of the base oil against NO $_{x}$ gas can be more increased by adding a phenol-based antioxidant and/or an organomolybdenum compound to the base oil.

Thus the second invention relates to a lubricating oil composition containing the base oil of the first invention and a phenol-based antioxidant and/or an organomelybdenum compound.

The phenol-based antioxidant to be used in the second invention is not critical and various compounds can be used. Representative examples of the phenol-based antioxidant are 4,4'-methylenebis(2,6-di-tert-butylphenol);

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- 4,4'-bis(2,6-di-tert-butylphenol);
- 4,4'-bis(2-methyl-6-tert-butylphenol);
- 2,2'-methylenebis(4-ethyl-6-tert-butylphenol);
- 2,2'-methylenebis(4-methyl-6-tert-butylphenol);
- 4,4'-butylidenebis(3-methyl-6-tert-butylphenol);
- 4.4'-isopropylidenebis(2.6-di-tert-buty/phenol);

10 . 17 51. (44) 2,2'-mèthylenebis(4-methyl-6-nonylphenol): ា នេះ ភាគ ស្រី៦ ភាគ ខា 2.2-methylenebis(4-methyl-6-cyclohexylphenol); 2.6-di-tert-butyl-4-methylphenol; was few and with The set 5 - 2,6-di-tert-butyl-4-ethylphenol; and the first see 1.5 cm of 5.5 cm of 5.5 cm of 5.5 cm. 3 7.7 2,4-dimethyl-6-tert-butylphenol; # = - 1 2,6-di-tert-α-dimethylamino-p-cresol; # = - 1 2.6-di-tert-butyl+4(N,N'-dimethylaminomethylphenol); 1334 134 144-thiobis(2-methyl-6-tert-butylphenol); a white a table of several replacement of a graph 7.6 → 70 (4,4'-thiobis(3-methyl-6-tert-butylphenol); which is a second of the second 2,2'-thiobis(4-methyl-6-tert-butylphenol); with the second control of the second control End that it bis(3-methyl-4-hydrexy-5-tert-butylbenzyl)sülfide; his has a passage of tert in the second of the seco 19-19-2015 bis(3,5-di-tert-butyl-4-hydroxybenzyl)sulfide, and the like. 🔻 🔞 🗀 🗃 🚉 🖽 🗀 🖼 🤊 🗀 🔻 🖽 🔻

The organomolybdenum compound to be used in the second invention is not critical and various is compounds can be used. As representative examples of the organomolybdenum compound, molybdenum dithiocarbamate (MoDTC), molybdenum dithiophosphate (MoDTP), and the like, which have been used as extreme pressure agents, can be used.

The amount of the phenol-based antioxidant and/or the molybdenum compound compounded varies with the properties of the base oil, the type of the phenol-based antioxidant or organomolybdenum compound and so forth, and cannot be determined unconditionally:

Usually, the phenol-based antioxidant and/or the organomolybdenum compound is compounded in the

When the phenol-based antioxidant alone is compounded, it is added in an amount of 0.05 to 3.0 parts by weight; preferably 0.1 to 2.0 parts by weight per 100 parts by weight of the base oil. When the organomolybdenum compound alone is compounded, it is added in an amount of 0.05 to 3.0 parts by weight, preferably 0.1 to 2.0 part by weight, most preferably 0.1 to 1.5 parts by weight per 100 parts by weight of the base oil. Similarly, when the phenol-based antioxidant and the organomolybdenum compound are compounded, they are added so that the amount of each of the phenol-based compound and the organomolybdenum compound compounded is 0.05 to 3.0 parts by weight, preferably 0.1 to 2.0 part by weight, most preferably 0.1 to 1.5 parts by weight per 100 parts by weight of the base oil.

In the second invention, when both the phenol-based antioxidant and the organomolybdenum compound are compounded, there is obtained a lubricating oil composition which exhibits much higher stability against NO_x gas than the compositions containing the phenol-based antioxidant or the organomolybdenum compound singly.

When both the phenol-based antioxidant and the organomolybdenum compound are compounded, they may be added in a suitable manner; for example, they are previously mixed and the resulting mixture is added to the base oil, or any one of them is first added to the base oil and then the other is added.

If necessary, various additives commonly used in the usual lubricating oil, such as Zn-DTP, a detergent dispersant, polymers and so forth, can be added to the base oil of the first invention and also to the lubricating oil composition of the second invention.

It has further been found that if a combination of a phenol-based antioxidant and an organomolybdenum compound is added to the general lubricating oil, the stability of the lubricating oil against NO_x gas is increased.

Thus the third invention relates to an additive for lubricating oil, consisting a phenol-based antioxidant and an organomolybdenum compound.

As the phenol-based antioxidant and the organomolybdenum compound, the compounds described in the second invention can be used. The additive consisting of a phenol-based antioxidant and an organomolybdenum compound of the third invention can be added in a suitable manner; for example, the phenol-based antioxidant and the organomolybdenum compound are previously mixed and the resulting mixture is added, or any one of them is first added and then the other is added.

The amount of the additive compounded varies with the properties of the lubricating oil, the type of each of the phenol-based antioxidant and the organomolybdenum compound, and so forth, and cannot be determined unconditionally. Usually the additive is added in such a manner that the amount of each of the phenol-based antioxidant and the organomolybdenum compound compounded is 0.05 to 3.0 parts by weight, preferably 0.1 to 2.0 parts by weight per 100 parts by weight of the base oil.

As the base oil for lubricating oil, the stability against NO_x gas of which can be improved by adding the additive of the third invention, those commonly used in the conventional lubricating oils, that is, mineral oil or synthetic oil having such properties as (1) proper viscosity characteristics, (2) good stability against

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oxidation, (3) good detergency and dispersancy, (4) good rust resistance and corrosion resistance, (5) good low temperature fluidity, and so forth can be used. More specifically, as the base oil for lubricating oil to be used in the third invention, the mineral oils and synthetic oils listed as the representative examples of the mineral oils and synthetic oils to be used in the first invention can be used.

In combination with the additive of the third invention, if necessary, other additives commonly used in the usual lubricating oil, such as Zn-DTP, a detergent dispersant, polymers and the like, can be added to the base oil for lubricating oil.

As described above, the base oil and the lubricating oil composition of the present invention are stable against NO_x gas and can be used effectively as a lubricating oil for internal compustion engines high in the NO_x gas concentration. They are useful not only as crank case oil for the usual gasoline engines and diesel engines but also as crank case oil for gas engines, that is, internal combustion engines using natural gas, liquefied petroleum gas (LPG), pyrolysis gas, coal decomposition gas, etc., vas the fuel.

The additive of the present invention, when added to abase oil for lubricating oil provides a lubricating oil stable against NO_x gas. Thus the additive can be used effectively in the production of lubricating oil for a high NO_x gas atmosphere in the production of lubricating oil for the internal combustion engines to be used the a high NO_x gas atmosphere in the production of lubricating oil for lubricat

the following examples. The present invention is described in greater detail with reference to the following examples.

The EXAMPLES 1 to 76 and COMPARATIVE EXAMPLES 1 to 45 had a sign of the sign o

Lubricating oils were prepared by mixing the base oils and additives shown in Table 1,...

These lubricating oil samples were subjected to the following NQ_x-degradation test.

Into 50 mt of the above subricating oil sample were blown nitrogen monoxide (NO)-gas (concentration, 196) and humidified air at rates of 6 thr and 40 st/hr, respectively, in the presence of an iron, copper catalyst (a test specimen specified in the oxidation test JIS K-2514). The temperature of the subricating oil sample was maintained at 135°C, and a time in which abnormal degradation (abrupt increase in acid value) started was measured as the induction period.

remain to The results are shown in Table.1. It is a comaginar to the gradual disease and a companient of the second of the secon

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^{*1} Phenol-based antioxidant (4,4'-methylenebis(2,6-di-tert-butylphenol): 1.1111

^{*2} Containing Zn-DTP, a metal-based detergent, an ashless dispersant, a polymer and the like.

⁵⁰ 3 Solvent purification oil (kinematic viscosity at 100°C: 4 cSt; viscosity index: 95, sulfur content: 500 ppm, aromatic content (% C_A): 8) obtained by subjecting a distillate oil from an intermediate base crude oil to solvent extraction-hydrogenation treatment.

^{*4} Solvent purification oil (kinematic viscosity, at 100°C: 4 cSt, viscosity, index: 100, sulfur content: 1000-ppm, aromatic content (% C_A): 4) obtained by subjecting a distillate oil from an intermediate base crude oil to solvent extraction-hydrogenation treatment.

[&]quot;5 Two-stage hydrogenated oil (kinematic viscosity at 100°C: 4 cSt, viscosity index: 100, sulfur content: 1 ppm, aromatic content (% C_A): not more than 2) obtained by subjecting a distillate oil from an intermediate base crude oil to two-stage hydrogenation treatment.

'6 Commercial available oil

Claims

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- 1. A base oil for lubricating oil, having a kinematic viscosity as determined at 100°C of 2 to 50 cSt, an aromatic content of not more than 2% and a viscosity index of at least 75.
- 2. The base oil as claimed in Claim 1, which is a deep dewaxed oil having a kinematic viscosity at 100°C of 2 to 50 cSt, an argmatic content of not more than 2%, a viscosity index of at least 75, a pour point 10 of not more than 20°C and a sulfur content of not more than 100 ppg.
 - 3. A lubricating oil composition comprising a base oil having a kinematic viscosity as determined at 100°C of 2 to 50 cSt and an aromatic content of not more than 2%, and a phenol-based antioxidant.
 - 4. The composition as claimed in Claim 3 wherein the amount of the phenol-based antioxidant compounded is from 0.05 to 3.0 parts by weight per 100 parts by weight of the base oil.
 - 5. The composition as claimed in Claim 3 wherein the amount of the phenol-based antioxidant compounded is from 0.05 to 2.0 parts by weight per 100 parts by weight of the base oil.
 - 6. A lubricating oil composition comprising a base oil having a viscosity as determined at 100°C of 2 to 50 cSt and an aromatic content of not more than 2%, and an organomolybdenum compound.
 - 7. The composition as claimed in Claim 6 wherein the amount of the organomolybdenum compound compounded is from 0.05 to 3.0 parts by weight per 100 parts by weight of the base oil.
 - 8. The composition as claimed in Claim 6 wherein the amount of the organomolybdenum compound, compounded is from 0.05 to 2.0 parts by weight per 100 parts by weight of the base oil.
 - 9. A lubricating oil composition comprising a base oil having a viscosity as determined at 100°C of 2 to 50 cSt and an aromatic content of not more than 2%, a phenol-based antioxidant and an organomolybdenum compound.
 - 10. The composition as claimed in Claim 9 wherein the amount of each of the phenol-based antioxidant and the organomolybdenum compound compounded is from 0.05 to 3.0 parts by weight per 100 parts by weight of the base oil.
- 11. The composition as claimed in Claim 9 wherein the amount of each of the phenol-based antioxidant 30 and the organomolybdenum compound compounded is from 0.05 to 2.0-parts by weight per 100 parts by weight of the base oil.
 - 12. The composition as claimed in Claim 3 or 9 wherein the phenol-based antioxidant is at least one compound selected from 4,4'-methylenebis(2,6-di-tert-butylphenol);
 - 4.4'-bis(2.6-di-tert-butylphenol);
- 35 4,4'-bis(2-methyl-6-tert-butylphenol);
 - 2,2'-methylenebis(4-ethyl-6-tert-butylphenol);
 - 2,2'-methylenebis(4-methyl-6-tert-butylphenol);
 - 4,4'-butylidenebis(3-methyl-6-tert-butylphenol);
 - ^ 4,4'-isopropylidenebis(2,6-di-tert-butylphenol):
 - 2,2'-methylenebis(4-methyl-6-nonylphenol);
 - 2.2'-isobutylidenebis(4.6-dimethylphenol);
 - 2,2'-methylenebis(4-methyl-6-cyclonexylphenol);
 - 2,6-di-tert-butyl-4-methylphenol;
 - 2,6-di-tert-butyl-4-ethylphenol;
- 45 2,4-dimethyl-6-tert-butylphenol;
 - 2,6-di-tert-α-dimethylamino-p-cresol;
 - 2,6-di-tert-butyl-4(N,N-dimethylaminomethylphenol);
 - 4,4'-thiobis(2-methyl-6-tert-butylphenol);
 - 4,4'-thiobis(3-methyl-6-tert-butylphenol);
- 50 2,2'-thiobis(4-methyl-6-tert-butylphenol);
 - bis(3-methyl-4-hydroxy-5-tert-butylbenzyl)sulfide and bis(3,5-di-tert-butyl-4-hydroxybenzyl)sulfide.
 - 13. The composition as claimed in Claim 6 or 9 wherein the organomolybdenum compound is at least one compound selected from molybdenum dithiocarbamate and molybdenum dithiophosphate.

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14. The composition as claimed in Claim 3, 6.or 9 wherein the base oil is a deep dewaxed oil having a kinematic viscosity at 100°C of 2 to 50 cSt, an aromatic content of not more than -20°C and a sulfur content of not more than 100 ppm.

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	15. An additive for a base oil for lub	pricating oil, consisting of a phenol-based antioxidant and a
	organomolybdenum compound.	A CONTRACTOR OF STREET OF STREET OF STREET
		wherein the phenol-based antioxidant is at least one compoun
	selected from 4,4'-methylenebis(2,6-di-tert-b	utylphenol);
5	4,4'-bis(2,6-di-tert-butylphenol);	9 4 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1
	4,4 -ois(2-metnyi-6-tert-butyiphenoi);	
	2,2'-methylenebis(4-ethyl-6-tert-butylphenol)	;
	2.2'-methylenebis(4-methyl-6-tert-butylpheno	
	4,4'-butylidenebis(3-methyl-6-tert-butylpheno	•
10	4,4'-isopropylidenebis(2,6-di-tert-butylphenol	n);
	2.2'-methylenebis(4-methyl-6-nonylphenol);	\$6.07.61 (1.1.1.1.1.1.1.1.1.1.1.1.1.1.1.1.1.1.1
	2.2'-isobutylidenebis(4,6-dimethylphenol);	
"\". و	2,2'-methylenebis(4-methyl-6-cyclohexylphe	nol);
	2,6-di-tert-butyl-4-methylphenol;	
15	2,6-di-tert-butyl-4-ethylphenol;	
	2,4-dimethyl-6-tert-butylphenol;	
	2,6-di-tert-α-dimethylamino-p-cresol;	
	2,6-di-tert-butyl-4(N,N'-dimethylaminomethyl	phenol);
***	4,4'-thiobis(2-methyl-6-tert-butylphenol);	, '
20:3	.4,4'-thiobis(3-methyl+6-tert-butylphenol);	STANDARD MARKATAN PARAMETER PARAMETER PARAMETER PARAMETER PARAMETER PARAMETER PARAMETER PARAMETER PARAMETER P Parameter Parameter
	2,2-thiobis(4-methyl-6-tert-butylphenol);	
	bis(3-methyl-4-hydroxy-5-tert-butylbenzyl)su	
	bis(3,5-di-tert-butyl-4-hydroxybenzyl)sulfide	15 wherein the organomolybdenum compound is at least one
-	17. The additive as claimed in Claim	15 wherein the organomolybdenum compound is at least one
25	compound selected from molybdenum dithic	ocarbamate and molybdenum dithiophosphate.
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EUROPEAN PATENT APPLICATION

- Application number: 88103563.8
- 2 Date of filing: 08.03.88

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- 43 Date of publication of application: 14.09.88 Bulletin 88/37 :
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- To acquire the -O- the Big Cot and (7) Applicant: IDEMITSUKOSAN COMPANY LIMITED No. 1-1, 3-chome, Marunouchi Chiyoda-ku Tokyo (JP)
 - (2) Inventor: Takao, Yabe c/o Idémitsu Kosan Co., Ltd. 24-4, Anesaki-kaigan lchihara-shi Chiba-ken (JP)
 - 7 Representative: Türk, Gille, Hrabal **Bruckner Strasse 20** D-4000 Düsseldorf 13 (DE)

to wordy that word you are the light, where the is

- Base oil for lubricating oil and lubricating oil composition containing said baid oil.
- A base oil for lubricating oil, a lubricating oil composition containing the base oil and a phenol-based antioxidant and/or an organomolybdenum compound, and also an additive for a base oil for lubricating oil, consisting of a phenol-based antioxidant and an organomolybdenum compound are disclosed. The base oil and the lubricating oil composition containing the base oil are stable against NOx gas and are useful for use in internal combustion engines. The additive, when added to a base oil, provides a lubricating oil which is stable against NOx gas and can be used effectively in a NOx gas atmosphere.

Bundesdruckerei Berlin



EP 88 10 3563

]	DOCUMENTS CONSIDERED TO BE RELEVANT	Γ	*	
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)	
X 3	FR-A-2 195 674 (SUN OIL COMPANY OF PENNSYLVANIA) * Page 1, line 25 - page 2, line 6; page 3, line 19 - page 4, line 22; page 5, lines 7-12; page 7, lines 13-27; page 7, example 1; page 8, example 2 *	1=5,12, 14	C 10 M 101/02 C 10 M 169/04 C 10 M 171/00 C 10 M 141/10 C 10 M 141/08 //	
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